Feb. 2, 1960 D. R. HALE ET AL 2,923,606

METHOD OF GROWING QUARTZ SINGLE CRYSTALS AND SEED BODY THEREFOR

Filed Sept. 6, 1955 2 Sheets-Sheet 1

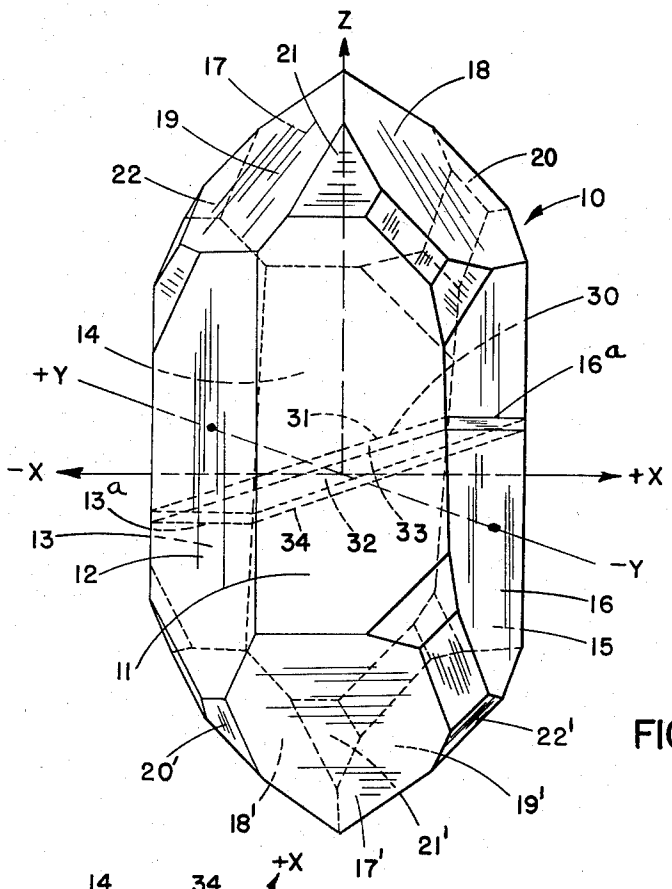


FIG. 1

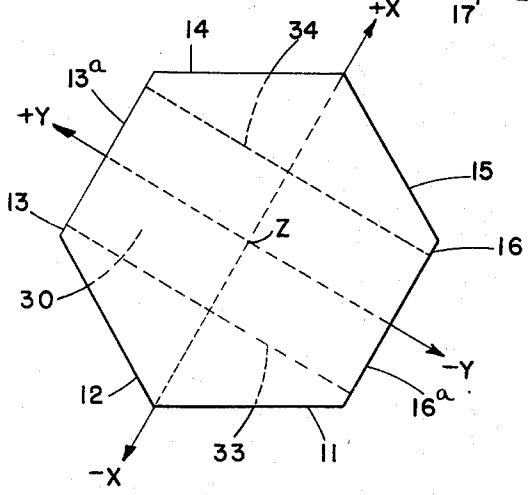


FIG. 2

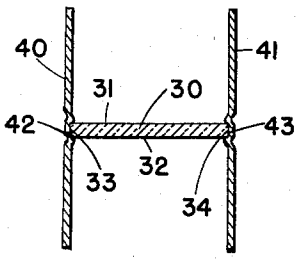


FIG. 3

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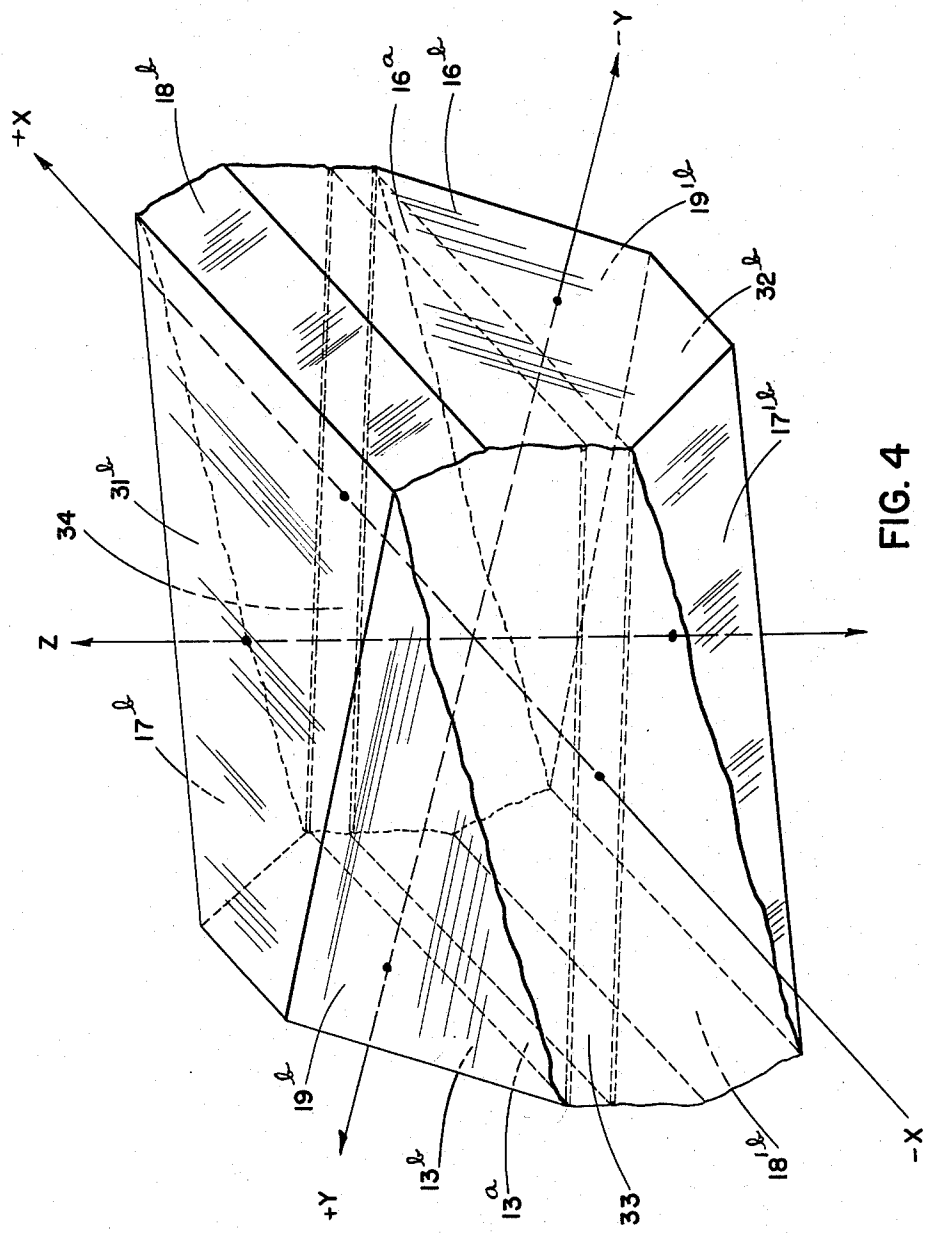


FIG. 4

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United States Patent Office 2,923,606 Patented Feb. 2, 1960

2,923,606

METHOD OF GROWING QUARTZ SINGLE CRYSTALS AND SEED BODY THEREFOR

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Application September 6, 1955, Serial No. 532,509

6 Claims. (Cl. 23—301)

This invention relates to the growing of artificial quartz single crystals.

Crystal plates of quartz have for many years been used extensively as frequency-determining elements in radio frequency oscillators, electrical filters, and the like. In consequence of the continuing demand for such crystal plates, considerable advances have been made in recent years in the synthesis of large single crystals of quartz from which such crystal plates may be fabricated. Illustrative of such advances are the apparatus and method described and claimed in U.S. Letters Patent 2,675,303 to Andrew R. Sobek and Danforth R. Hale, assigned to the same assignee as the present invention. In accordance with the general procedure of this patent, successful synthesis of single crystals of quartz has been obtained by exposing a quartz crystal seed under conditions of elevated temperature and pressure to an aqueous medium containing substantial quantities of an alkali metal carbonate, such as sodium carbonate. The alkaline aqueous medium is maintained in contact with a supply material of crystalline quartz and crystal growth takes place by the transfer of silica from the supply material to the quartz seed. Other methods have also been employed with success in which the quartz seed is exposed to other suitable predetermined chemical and physical environments which promote crystalline growth on the seed to produce a quartz crystal bar from which crystal plates may be fabricated.

An important practical consideration in growing artificial quartz single crystals is the desirability of obtaining a high yield of quartz usable for crystal plates from a given autoclave in a given time. The achievement of an appreciably increased rate of growth of usable crystal material results in a corresponding reduction in the cost per crystal plate. In this connection it is emphasized that, in addition to a high growth rate, an equally important desideratum is the production of crystals which have a shape most suited to the fabrication of crystal plates. Thus a high growth rate alone is not sufficient because if the resulting crystal is of irregular shape as caused by the formation of natural faces intersecting at acute angles, much of the crystal material is wasted in cutting plates and the high growth rate is of little more than academic significance.

In accordance with the present invention an optimum combination of increased growth rate and a regularly-shaped crystal substantially resembling a rectangular parallelepiped in configuration is achieved by the use of a novel seed plate oriented, with respect to the mother crystal, so that its opposite planar major surfaces are inclined at an angle of about $+70\pm7°$ or $-70\pm7°$ to the crystallographic Z-axis and extend substantially parallel to a crystallographic X-axis. In conformity with established convention, the seed plate of the invention may be designated as a $(yzw)\phi$ or $(yx1)\phi$ plate where the orientation angle ϕ is equal to $\pm70\pm7°$.

It is, therefore, an object of this invention to provide a novel and improved method of growing single crystals of quartz which results in an improved yield of usable crystal material per unit of growing time.

It is also an object of the present invention to provide a novel and improved method of growing single crystals of quartz by the deposition of quartz from an aqueous solution onto a quartz seed body in which quartz is deposited on the seed body at an increased rate and in such a manner as to form a crystal of highly efficient shape for crystal plate fabrication.

Another object of this invention is to provide a novel quartz seed body which promotes faster growth of a quartz single crystal by the deposition of quartz from a transfer medium onto the seed body and which grows to a crystal having a configuration resembling a rectangular parallelepiped.

Other and further objects and advantages of the present invention will be apparent from the following description of the preferred embodiment thereof, disclosed in detail in the following description referring to the accompanying drawings.

In the following discussion the standards adopted in the "Standards on Piezoelectric Crystals" (1949) of the Institute of Radio Engineers, set forth in the Proceedings of the I.R.E., vol. 37, pp. 1378–1395, are followed.

In the drawings:

Figure 1 is a perspective view showing an idealized full grown, large natural single crystal of quartz of the left-handed variety and showing the orientation with respect thereto of a quartz seed plate representing one particular embodiment of the present invention;

Figure 2 is a transverse section through the Fig. 1 mother quartz, taken perpendicular to the crystallographic Z-axis and showing in dashed-line outline the exemplary seed plate illustrated in Fig. 1;

Figure 3 is a transverse section through a holder and seed plate assembly for growing a crystal in accordance with the present invention; and

Figure 4 is an enlarged perspective view of a quartz crystal grown in accordance with the present invention.

Referring to Fig. 1, there is shown an idealized natural crystal **10** of left-handed quartz. As is well understood, this crystal is elongated in the direction of the crystallographic Z-axis. At its middle the crystal is bounded by the six primary prism faces **11–16** characterized in crystallography by their Miller index $\{10\bar{1}0\}$. These primary prism faces extend parallel to the crystallographic Z-axis, which is the direction of natural elongation of quartz. Each of these prism faces is intersected by a pair of neighboring primary prism faces, each inclined at 60° thereto. At one end, in the direction of the crystallographic Z-axis, there are three intersecting major rhombohedral faces, identified by the reference numerals **17, 18** and **19** in Fig. 1. The Miller index for these major rhombohedral faces, as well as for their counterparts **17′, 18′**, and **19′** at the opposite end of the crystal, is $\{10\bar{1}1\}$. Minor rhombohedral faces **20, 21, 22** and **20′, 21′, 22′** of Miller index $\{01\bar{1}1\}$ are located between the major rhombohedral faces. Fig. 1 shows certain additional faces, which sometimes occur in natural quartz crystals but which are not important for an understanding of the present invention.

In accordance with the present invention there is provided a novel seed plate cut from the mother quartz.

Referring to Fig. 1, there is shown one seed plate **30** which is a specific embodiment of the generic invention. According to established standards of designation seed plate **30** will be referred to as a $(yzw)\phi$ cut. In a $(yzw)\phi$ plate the plane of the plate contains or is parallel to a crystallographic X-axis and the orientation angle, i.e., the angle which the plane makes with the crystallographic Z-axis is designated by ϕ. For seed plate **30**,

which will be described in detail by way of example, the angle ϕ is $+72°23'$. However, in accordance with the present invention, ϕ may be any angle in the range $+70°\pm7°$ and $-70°\pm7°$.

Referring once again to Fig. 1, the illustrated seed plate **30** has opposite planar major surfaces **31** and **32**, rectangular in form, and opposite end surfaces **13***a* and **16***a* which extend parallel to the aforesaid crystallographic X-axis. In the exemplary embodiment, end edges **13***a* and **16***a* of the seed plate **30** are portions respectively of the major prism faces **13** and **16** of the mother crystal **10** and the side edges **33** and **34** of the plate extend between the end edges **13***a* and **16***a* and perpendicular to said crystallographic X-axis. It will be understood, however, that the size and plan configuration of the seed plate may be selected in accordance with the desired dimensions of the crystal to be grown.

As previously mentioned and hereinafter pointed out with greater particularity, seed plates according to the present invention are characterized not only by a higher growth rate but also by a far more efficient shape (being block-like in form) for cutting into plates than conventional seeds such as minor rhombohedral plates or cuts at other orientations than those specified herein. For example, if a seed plate having opposite major surfaces each lying in an atomic plane inclined at $-52°41'$ to the crystallographic Z-axis and extending parallel to a crystallographic X-axis is used, these major surfaces rapidly disappear in favor of major rhombohedral faces, rather than maintaining themselves throughout the growth of the crystal. The formation of major rhombohedral faces on quartz crystals tends to taper the crystal and reduce the growing area, and thus not only reduces the over-all crystal growth rate (in terms of weight per unit time) but also yields a grown crystal having a poor shape for cutting. These disadvantageous results are appreciably avoided in the present invention.

It has been determined that an increased growth rate in terms of dimensional increase per day perpendicular to the major seed surfaces takes place on the present seed plates, as compared with the crystal growth of a seed plate having major surfaces parallel to a minor rhombohedral crystal face, which is the quartz seed plate in most common use in this country. This dimensional increase tends to result in an increased weight of crystal material deposited. In addition, throughout the growth of a crystal on the present seed plate the major surfaces on which crystal growth is taking place remain relatively large in size since these major surfaces extend at relatively large angles to the major rhombohedral crystal faces and therefore the major rhombohedral faces do not rapidly decrease the size of these growing faces as crystal growth proceeds. Accordingly, the dimensional increase just mentioned takes place uniformly across these relatively large major surfaces, with the result that the weight increase, as compared with the minor rhombohedral seed plate, is very appreciable. In one particular run for example, this weight increase amounted to 44%. What is equally important is the regular, block-like shape of the grown crystal as shown in Figure 4.

In growing the crystal from the present seed plates, the seed plate **30**, for example, is supported by a suitable holder engaging the side edges **33** and **34** on the seed plate, leaving the seed plate free and unconfined at its end edges **13***a* and **16***a* and at its major surfaces **31** and **32**. A suitable holder arrangement for this purpose is shown in Fig. 3, comprising a pair of spaced parallel, flat walls **40** and **41** deformed to provide shallow grooves **42** and **43** in their confronting faces. The seed plate is positioned with its side edges **33** and **34** received in these grooves. It will be apparent that as crystal growth takes place on the seed plate the holder walls **40** and **41** confine the crystal against growth outward from its side edges. The crystal seed thus supported is exposed to an alkaline aqueous solution in contact with a supply of crystalline quartz and under conditions of elevated temperature and pressure which maintain a condition of supersaturation of quartz around the seed plate to promote crystal growth thereon. For example, the particular physical and chemical conditions described in the above-mentioned Patent 2,675,303 may be employed. As the crystal growth proceeds the crystal surfaces on which crystal growth is taking place maintain themselves generally parallel to the original surfaces.

Referring to Fig. 4, wherein there is shown a crystal grown from the particular exemplary seed plate, shown in Fig. 1, the top surface **31***b* on the crystal is inclined at $+72°23'$ to the crystallographic Z-axis and extends parallel to a crystallographic X-axis. This crystal surface is somewhat smaller in size than the corresponding major surface **31** on the seed plate from which the crystal was grown, particularly toward the left end of the crystal in Fig. 4 due to the formation of the major rhombohedral faces **19***b* and **17***b* which taper the crystal in the X-axis direction. These major rhombohedral faces correspond to the major rhombohedral faces **19** and **17** on the mother quartz. At the right end of the crystal in Fig. 4 the top surface **31***b* is somewhat shorter than the seed plate in the direction parallel to the side edges **33** and **34** of the seed plate due to the formation of the major rhombohedral crystal face **18***b*, which corresponds to the major rhombohedral face **18** on the mother quartz. At the bottom half of the crystal the major rhombohedral faces **17'***b* and **19'***b*, which correspond to the major rhombohedral faces **17'** and **19'** on the mother quartz, reduce the size of the crystal in the X-axis direction progressively toward the right end. At the left end of the crystal the major rhombohedral face **18'***b*, which corresponds to the major rhombohedral face **18'** on the mother quartz, reduces the length of the bottom half of the crystal bar in the direction parallel to the side edges **33** and **34** of the seed plate. The end faces **16***b* and **13***b* on the Fig. 4 crystal are prism faces and are extensions of the end faces **16***a* and **13***a* on the seed plate from which this crystal was grown. The holder for the seed plate has confined the crystal against any growth in the X-axis direction, so that crystal growth has taken place only perpendicular to the major surfaces **31** and **32** on the seed plate. Crystals grown from the other seed plates coming within the scope of the invention, viz., $\phi=+70\pm7°$ and $-70\pm7°$ are similar in appearance and growth rate to that illustrated in Fig. 4.

It is to be noted that, in addition to having a rapid growth rate, the crystal grown in accordance with the present invention has a relatively efficient shape for the fabrication of oscillator blanks since the tapering imposed by the partially formed major rhombohedral faces is not severe.

It is to be understood that, while the present invention has been described with particular reference to the seed plate having its major surfaces inclined at $+72°23'$ to the crystallographic Z-axis, plates having $\phi=-72°23'$ are equally advantageous and all plates in the range $\phi=+63$ to $+77$ and -63 to -77 are fully operative and within the scope of the invention as providing unusually high growth rates and desirable crystal shapes. In addition, slight deviations in orientation relative the crystallographic X- and Y-axes are permissible without substantial detriment to the advantageous results of this invention. Accordingly, such minor changes are considered to fall within the spirit and scope of the present invention. Furthermore, it is to be understood that the present invention is adapted for use in the synthesis of quartz under any chemical and physical environment found suitable for this purpose, even though differing from the particular growing environment mentioned herein.

The present application is a continuation-in-part of a copending application Serial No. 459,016, filed on September 29, 1954, and subsequently abandoned.

We claim:

1. A method of growing a quartz single crystal in a predetermined chemical and physical environment which promotes quartz crystal growth, which method comprises the steps of: providing a quartz seed consisting of a $(yzw)\phi$ cut quartz plate where ϕ is the angle said plate makes with the crystallographic Z-axis and is within the range $\pm 70° \pm 7°$; supporting the seed plate unconfined against growth on its major surfaces; and exposing the seed plate, while thus supported, to said chemical and physical environment to cause crystal growth on the seed body.

2. The method defined in claim 1 wherein the angle ϕ is in the range $+63°$ to $+77°$.

3. The method defined in claim 1 wherein the angle ϕ is in the range $-63°$ to $-77°$.

4. A method of growing a quartz single crystal by the deposition of quartz from a growing medium onto a quartz seed which comprises the steps of: providing a quartz seed plate having opposite major surfaces inclined at an angle ϕ to the crystallographic Z-axis and extending substantially parallel to a crystallographic X-axis and having opposite side edges extending substantially perpendicular to said crystallographic X-axis, said angle ϕ being in the range $\pm 70° \pm 7°$; confining the seed plate against substantial crystal growth beyond said side edges; and exposing said seed plate, while thus confined, to a growing medium which provides supersaturation of quartz in the neighborhood of the seed plate to cause crystal growth on the seed plate outward from said major surfaces thereof.

5. A method of growing a quartz single crystal by the deposition of quartz from an aqueous transfer medium onto a quartz seed which comprises the steps of: providing a quartz seed plate having opposite planar major surfaces inclined at an angle of about $\pm 70° \pm 7°$ to the crystallographic Z-axis and extending parallel to a crystallographic X-axis, opposite end edges extending substantially parallel to said crystallographic X-axis, and side edges extending perpendicular to said crystallographic X-axis between said end edges at opposite sides of the seed plate; supporting the seed plate at said side edges

thereof to confine the seed plate against crystal growth on its sides and leaving the seed plate unconfined against crystal growth on its major surfaces; and exposing said seed plate, while thus supported, to an aqueous transfer medium in contact with a supply or silica under conditions of elevated temperature and pressure which provide supersaturation of quartz in said medium around the seed plate to promote crystal growth on the seed plate outward from said major surfaces on the seed plate.

6. A method of growing a quartz single crystal by the deposition of quartz from an alkaline aqueous growing solution onto a quartz crystal seed which comprises the steps of: providing a quartz seed plate having opposite planar major surfaces inclined at substantially $\pm 72°23'$ to the crystallographic Z-axis and extending parallel to a crystallographic X-axis, opposite end edges extending substantially parallel to said crystallographic X-axis, and side edges extending perpendicular to said crystallographic X-axis between said end edges at opposite sides of the seed plate; supporting the seed plate at said side edges thereof between spaced walls which prevent crystal growth outward from said side edges of the seed plate; and exposing said seed body, while thus supported, to an alkaline aqueous solution in contact with a supply of crystalline quartz and under conditions of elevated temperature and pressure which establish supersaturation of quartz in the solution adjacent the seed plate to cause crystal growth on the seed plate.

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